［無機・分析化学標準］

以下の問（1）～（4）に答えよ．
なお，原子番号は $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{27}$Co, $_{28}$Ni, $_{29}$Cu である．

（1）化学組成の分析に用いる以下二つの機器分析法について，問(a), (b)に答えよ．

・誘導結合プラズマ発光分析 (ICP-AES)
・蛍光 X 線分析 (XRF)

(a) 測定原理をそれぞれ 100 字程度で説明せよ．
(b) それぞれの手法特有の長所を挙げよ．

（2）Cr, Mn, Fe における中性のカルボニル (CO) 錯体について，問(c), (d)に答えよ．
(c) $Cr^{(0)}$, $Mn^{(0)}$, $Fe^{(0)}$の CO 錯体は全て 18 電子則を満たす．それぞれの分子式を記せ．
(d) (c)における CO 錯体の立体構造を，図 1 の例にならってそれぞれ示せ．

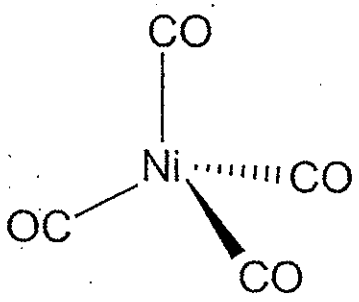

図 1．$Ni(CO)_4$ 錯体の立体構造．

（3）Fe と Co の八面体錯体について，以下の問(e)～(h)に答えよ．
(e) 5 重に縮退する遷移金属の 3d 軌道 (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}) は，正八面体配位の結晶場により，e_g軌道と t_{2g}軌道の二つに分裂する．このとき，Fe^{3+}と Co^{3+}の取りうる d 電子配置を全て図示せよ．なお，d 電子数に注意し，各電子のスピンの向きを矢印(↑, ↓)で区別すること．
(f) K_3FeF_6, $K_3[Fe(CN)_6]$, $K_3[Co(CN)_6]$の三つの錯体塩の磁気特性を調べたところ，遷移金属イオンあたりの常磁性磁気モーメントが A: 0.0 μ_B, B: 2.3 μ_B, C: 5.9 μ_B であった．なお，μ_B はボーア磁子である．どの錯体塩が A, B, C に該当するか同定せよ．また，判断した根拠を 150 字程度で説明せよ．
(g) $[Fe(NCS)(H_2O)_5]^{2+}$を含む溶液に NaF 粉末を加えたところ，NCS^-と F^-の間で配位子交換が起こった．この配位子交換反応が進行する理由を Hard and Soft Acids and Bases (HSAB) 則にもとづいて 50 字程度で説明せよ．

(h) (g)における配位子交換反応が完了すると，溶液の色が血赤色からほぼ無色へと変化した．この色の変化の理由を，次の三つの語句を用いて 150 字程度で説明せよ．

［語句］

・LMCT 遷移　(注:「LMCT」は Ligand-to-Metal Charge Transfer の略)

・d–d 遷移

・電気陰性度

（4）Cu^{2+}の錯体・結晶について以下の問(i), (j)に答えよ．

(i) $[Cu(en)_2]^{2+}$ (en: ethane-1,2-diamine) は$[Cu(NH_3)_4]^{2+}$と類似した平面四角形の配位構造を持つ．この二つの錯体を比較すると，$[Cu(en)_2]^{2+}$の方が高い安定性を示す．この安定性の違いを生じる効果の名称を記せ．また，$[Cu(en)_2]^{2+}$の方が安定となる理由を熱力学的な観点から 50 字程度で説明せよ．

(j) 八面体配位の基本骨格を有するCu^{2+}の酸化物やフッ化物の結晶では，周期表で隣接する Fe^{2+}, Co^{2+}, Ni^{2+}と比較して，対称性の低い結晶構造をとることが多い．その理由を，Cu^{2+}の八面体配位の電子配置にもとづいて 100 字程度で記せ．なお，図を用いて説明してもよい．図に使用する文字は文字数には含めないものとする．

Answer the following problems (1) through (4).

The atomic numbers are $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{27}$Co, $_{28}$Ni, and $_{29}$Cu.

(1) Answer the problems (a) and (b) regarding the following two methods for chemical composition analysis.

- Inductively coupled plasma atomic emission spectroscopy (ICP-AES)
- X-ray fluorescence spectroscopy (XRF)

(a) Explain the measurement principles in approximately 50 words each.

(b) List the unique advantage of each.

(2) Answer the problems (c) and (d) regarding neutral Cr, Mn, and Fe carbonyl (CO) complexes.

(c) All CO complexes of $Cr^{(0)}$, $Mn^{(0)}$ and $Fe^{(0)}$ satisfy the 18-electron rule. Show each molecular formula.

(d) Illustrate the three-dimensional structures of each CO complex in (c), following the example in Figure 1.

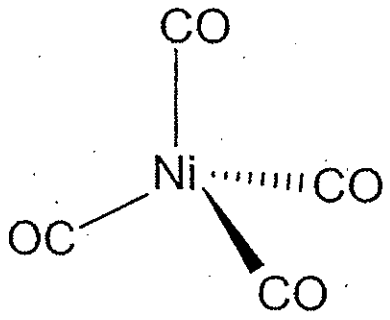

Figure 1. Three-dimensional structure of the $Ni(CO)_4$ complex.

(3) Answer the problems (e) through (h) regarding the octahedral complexes of Fe and Co.

(e) Under the crystal field of a regular octahedral coordination, the 5-fold degeneracy of transition metal 3d orbitals (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}) is lifted, splitting into two sets: e_g orbitals and t_{2g} orbitals. Illustrate all possible d-electron configurations for Fe^{3+} and Co^{3+}, paying attention to the number of d-electrons and distinguishing the spin direction of each electron with arrows (↑, ↓).

(f) When investigating the magnetic properties of K_3FeF_6, $K_3[Fe(CN)_6]$, and $K_3[Co(CN)_6]$, the paramagnetic moments per transition metal ion were found to be A: 0.0 μ_B, B: 2.3 μ_B, and C: 5.9 μ_B, where μ_B is the Bohr magneton. Identify which complexes correspond to A, B, and C. Furthermore, explain the reason behind your determination in approximately 75 words.

(g) When NaF powder was added to a solution containing $[Fe(NCS)(H_2O)_5]^{2+}$, ligand exchange occurred between NCS^- and F^-. Based on the hard and soft acids and bases (HSAB) theory, explain in approximately 30 words why this exchange reaction between NCS^- and F^- preferably proceeds.

(h) After the ligand exchange reaction described in (g) was completed, the color of the solution changed from blood-red to nearly colorless. Explain the reason for this color change using the following three terms in approximately 75 words.

[Terms]

- LMCT transition (Here, "LMCT" stands for Ligand-to-Metal Charge Transfer.)
- d–d transition
- Electronegativity

(4) Answer the problems (i) and (j) regarding the Cu^{2+} complexes and crystals.

(i) $[Cu(en)_2]^{2+}$(en: ethane-1,2-diamine) exhibits a planar square coordination structure similar to $[Cu(NH_3)_4]^{2+}$. Comparing the two complexes, $[Cu(en)_2]^{2+}$ is more stable. Answer the name of the effect that causes this stability difference. Furthermore, explain why $[Cu(en)_2]^{2+}$ is more stable thermodynamically in approximately 30 words.

(j) Compared to Fe^{2+}, Co^{2+}, and Ni^{2+}, which are adjacent in the periodic table, Cu^{2+} oxides or fluorides with an octahedral coordination geometry often exhibit lower symmetry crystal structures. Explain the reason based on the electron configuration of Cu^{2+} octahedral coordination in approximately 50 words. You may use figures for explanation and words used in the figures are not counted towards the word limit.